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(54) COPPER ALLOY AND COPPER ALLOY THIN SHEET EXHIBITING IMPROVED WEAR OF BLANKING METAL MOLD

(57) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, and solderability as well as excellent resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and, if required, further containing 0.003 to 0.5 weight % of Ni and 0.003 to 0.5 weight % of Sn, and further containing a total amount of 0.0007 to 0.5 weight % of one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si, and the balance being Cu and inevitable impurities, in which the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.

Description

Technical Field

5 [0001] This invention relates to a copper-based alloy having a small blanking die wear property (hereinafter referred to as "blanking die wear resistance") and a copper-based alloy and sheet thereof having excellent blanking die wear resistance and resin adhesion.

10 [0002] Further, this invention relates to a copper-based alloy having excellent repeated bending fatigue resistance and excellent solderability, and to a copper-based alloy and sheet thereof having excellent repeated bending fatigue resistance and excellent solderability, as well as having excellent blanking die wear resistance and resin adhesion.

Background Art

15 [0003] Generally, lead frames for semiconductor devices, such as ICs and LSIs, and terminals and connectors for various electrical and electronic parts, are manufactured by cutting a copper-based alloy sheet into strips, which are then subjected to metal working, such as punching, pressing and bending. Lead frames of many kinds of semiconductor devices as well as many kinds of terminals and connectors are used in resin packaging with thermosetting resin.

[0004] The copper-based alloy sheets which are known to be used to manufacture these lead frames for semiconductor devices include:

20 [0005] A copper-based alloy sheet consisting essentially of 0.05 to 3.5 weight % of Fe, 0.01 to 0.4 weight % of P, and the balance of Cu and inevitable impurities;

[0006] A copper-based alloy sheet consisting essentially of one or two elements selected from the group consisting of 0.05 to 3.5 weight % of Fe, 0.01 to 0.4 weight % of P, 0.05 to 5 weight % of Zn, and 0.05 to 5 weight % of Sn, and the balance of Cu and inevitable impurities;

25 [0007] A copper-based alloy sheet consisting essentially of 0.05 to 3.5 weight % of Fe, 0.01 to 0.4 weight % of P, 0.01 to 2 weight % in total one or two or more elements selected from the group consisting of Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and B, and the balance of Cu and inevitable impurities; and

[0008] A copper-based alloy sheet consisting essentially of one or two elements selected from the group consisting of 0.05 to 3.5 weight % of Fe, 0.01 to 0.4 weight % of P, 0.05 to 5 weight % of Zn, and 0.05 to 5 weight % of Sn, and further containing 0.01 to 2 weight % in total one or two or more elements selected from the group consisting of Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and B, and the balance being Cu and inevitable impurities (Japanese Laid-Open Patent Publication (Kokai) No. 9-296237).

35 [0009] In recent years, semiconductor devices such as ICs and LSIs have become higher in packing density and smaller in size, and lead frames used in these semiconductor devices have become reduced in thickness, increased in number of pins and narrower in pitch. Further, many high accuracy terminals and connectors which are compact in size and reduced in thickness have become used to support various electrical and electronic parts which have become higher in performance. Important factors to support the manufacture of these lead frames which have become reduced in thickness, with more pins and narrower pitch, and high accuracy terminals and connectors which have become compact in size and reduced in thickness, include dimensional tolerance and the size of burrs. If the blankability of the processing material is poor, the mold will wear after a short usage. When the mold wears, the dimensional tolerance decreases, resulting in greater burrs which make it impossible to provide the terminals and connectors with more pins and narrower pitch. Blanking of conventional copper-based alloy sheets was prone to cause heavy wearing of the mold, and hence the mold had to be exchanged after a short usage. This led to high costs, and to reduce the cost, a copper-based alloy sheet having more excellent blanking die wear resistance is desired.

45 [0010] Further, pins on the ICs, LSIs and the like tend to bend during handling when the ICs, LSIs and the like are being manufactured. Moreover, in many cases, semiconductor devices on the market are used for special applications or re-used. In such cases, it is necessary to rectify the pins of the semiconductor devices by repeated bending. These pins of the semiconductor devices with reduced thickness and narrower pitch can occasionally break during the repeated bending process due to fatigue. When the pins break, the semiconductor devices can no longer be used and must be disposed, thus resulting in a tremendous decrease in productivity. Therefore, there is demand for a copper-based alloy sheet having such excellent resistance to fatigue during repeated bending that it will not break during the repeated bending process.

55 [0011] Further, the lead frames for semiconductor devices, and the terminals and connectors for various electrical and electronic parts are usually soldered, and the soldering area is more strongly required to be smaller and the soldering temperature and time are required to be as low and short as possible. Moreover, because activated flux used in soldering accelerates corrosion, in recent years, low activated or non-activated flux is becoming used for soldering the lead frames, terminals and connectors. However, when the lead frames, terminals and connectors of poor soldering materials are soldered with a low activated or non activated flux and over the small soldering area, an incomplete sol-

dering can occur. This is one of the reasons that the product has spoiled reliability, and thus a copper-based alloy sheet with further improved solderability is desired.

[0012] Further, semiconductor chips such as ICs and LSIs are subjected to die-bonding and wire-bonding at approximately 200°C or higher temperatures and then are resin packaged for protection from the external environment. Molding for the resin packaging is conducted at a temperature of 160°C or higher, but if the adhesion strength of the resin and the lead frames is weak, then separation of the resin and the lead frames can occur. A device with such separation undergoes moisture absorption and the package can occasionally break during the following reflow soldering process due to the vapor pressure of the moisture. This problem has been a serious obstacle to fulfillment of severe reliability requirements.

[0013] Therefore, it is an object of this invention to provide a copper-based alloy having excellent blanking die wear resistance.

[0014] Another object of this invention is to provide a copper-based alloy having excellent blanking die wear resistance as well as excellent high resin adhesion.

[0015] A further object of this invention is to provide a copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability.

[0016] Another object of this invention is to provide a copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability as well as excellent high resin adhesion.

Disclosure of the Invention

[0017] To solve the aforesaid problems, the present inventors have made studies and have reached the following findings:

(a) Blanking die wear resistance is greatly affected by carbon and carbide in a Fe-Zn-P copper-based alloy with Fe, Zn and P in copper which is used to manufacture lead frames for semiconductor devices, and terminals and connectors for various electrical and electronic parts. Especially, when 0.0005 to 0.02 weight % of C (preferably 0.001 to 0.02 weight % of C) is added to a conventional Fe-Zn-P copper-based alloy having a composition of 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and the balance of Cu and inevitable impurities, blanking die wear resistance is further improved over the conventional Fe-Zn-P copper-based alloy;

(b) When one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si, are added in an amount of 0.0007 to 0.5 weight % in total, to the above-mentioned Fe-Zn-P copper-based alloy under paragraph (a) having excellent blanking die wear resistance, consisting essentially of 1.5 to 2.4 weight % of Fe, 0.008 to 0.8 weight % of P, 0.01 to 0.50 weight % of Zn, as well as 0.0005 to 0.02 weight % of C, and the balance of Cu and inevitable impurities, resin adhesion is further improved over the conventional Fe-Zn-P copper-based alloys;

(c) Resin adhesion is further improved when one element of the above mentioned Al, Be, Ca, Cr, Mg and Si is added in an amount of 0.0007 to 0.5 weight %. However, adding Mg and Si is most preferred. Either Mg or Si may be added in an amount of 0.0007 to 0.5 weight % of Mg or 0.0007 to 0.5 weight % of Si, or both Mg and Si may be added in the amounts of 0.0007 to 0.5 weight % of Mg and 0.0007 to 0.5 weight % of Si, so that Mg and Si coexist in the alloy; and

(d) When the above-mentioned Fe-Zn-P copper-based alloys as described under paragraph (a), (b) or (c), with addition of 0.0005 to 0.02 weight % of C (preferably 0.001 to 0.02 weight % of C), contains one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo (hereinafter these elements will be referred to as "the carbide-forming elements") in a total amount equal to or more than 0.01 weight %, the action of enhancing the blanking die wear resistance by the added carbon is suppressed. Therefore, the total content of the one or two or more carbide-forming elements should preferably be limited to less than 0.01 weight %.

[0018] The present invention is based upon the above findings, and is characterized by:

(1) A copper-based alloy having excellent blanking die wear resistance comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, 0.0005 to 0.02 weight % of C, and the balance of Cu and inevitable impurities;

(2) A copper-based alloy having excellent blanking die wear resistance comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, 0.001 to 0.02 weight % of C, and the balance of Cu and inevitable impurities; and

(3) A copper-based alloy as described under paragraph (1) or (2), having excellent blanking die wear resistance, in which the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.

The resin adhesion of the above mentioned copper-based alloy having excellent blanking die wear resistance con-

taining 0.0005 to 0.02 weight % of C, is improved when one element selected from the group consisting of Al, Be, Ca, Cr, Mg and Si is added in an amount of 0.0007 to 0.5 weight % of Al, 0.0007 to 0.5 weight % of Ca, 0.0007 to 0.5 weight % of Be, 0.0007 to 0.5 weight % of Cr, 0.0007 to 0.5 weight % of Mg or 0.0007 to 0.5 weight % of Si. Alternatively, two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si may be added in a total amount of 0.0007 weight % to 0.5 weight %. Among the group consisting of Al, Be, Ca, Cr, Mg and Si, it is preferable to add Mg and Si, and also preferably either Mg or Si may be added in an amount of 0.0007 weight % to 0.5 weight % of Mg, or 0.0007 weight % to 0.5 weight % of Si. However, it is possible to add both Mg and Si in amounts of 0.0007 weight % to 0.5 weight % of Mg and 0.0007 weight % to 0.5 weight % of Si so that Mg and Si coexist in the alloy.

Therefore, this invention is characterized by:

(4) A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si in a total amount of 0.0007 to 0.5 weight %, and the balance being Cu and inevitable impurities;

(5) A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and the balance being Cu and inevitable impurities;

(6) A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Si, and the balance being Cu and inevitable impurities;

(7) A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and 0.0007 to 0.5 weight % of Si, and the balance being Cu and inevitable impurities;

(8) A copper-based alloy as described under any of paragraphs (4), (5), (6) and (7) having excellent blanking die wear resistance and resin adhesion, in which C is contained in an amount of 0.001 to 0.02 weight %; and

(9) A copper-based alloy as described under any of paragraphs (4), (5), (6), (7) and (8) having excellent blanking die wear resistance and resin adhesion, in which the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.

The copper-based alloys described under paragraphs (1), (2), (3), (4), (5), (6), (7), (8) and (9) are intended to be used in the form of sheets.

Therefore, this invention is characterized by:

(10) A copper-based alloy sheet formed of the copper-based alloy described under any of paragraphs (1), (2), (3), (4), (5), (6), (7), (8) and (9).

Further, the present inventors made further studies and have reached the following findings:

(e) Repeated bending fatigue resistance and solderability is improved when 0.003 to 0.5 weight % of Ni and 0.003 to 0.5 weight % of Sn are added to the conventional Fe-Zn-P copper-based alloy comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.8 weight % of P, 0.01 to 0.50 weight % of Zn, and the balance of Cu and inevitable impurities, which is used to manufacture lead frames for semiconductor devices, and terminals and connectors for various electrical and electronic parts. Further, blanking die wear resistance is improved by adding 0.0005 weight % to 0.02 weight % of C (preferably 0.001 weight % to 0.02 weight % of C);

(f) Resin adhesion is improved when one or two or more elements selected from the group of Al, Be, Ca, Cr, Mg and Si are added in an amount total of 0.0007 to 0.5 weight %, to the Fe-Zn-P copper-based alloy described under paragraph (e), comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.8 weight % of P, 0.01 to 0.50 weight % of Zn, and the balance of Cu and inevitable impurities, which has excellent blanking die wear resistance, repeated bending fatigue resistance and solderability;

(g) Resin adhesion is further improved when one element of the above-mentioned Al, Be, Ca, Cr, Mg and Si is added in an amount of 0.0007 to 0.5 weight %. Particularly, adding Mg and Si is most preferred. Either Mg or Si may be added in an amount of 0.0007 to 0.5 weight % of Mg or 0.0007 to 0.5 weight % of Si, or both Mg and Si may be added in amounts 0.0007 to 0.5 weight % of Mg and 0.0007 to 0.5 weight % of Si so that Mg and Si coexist in the alloy; and

(h) The Nb, Ti, Zr, Ta, Hf, W, V and Mo (hereinafter these elements will be referred to as "the carbide-forming elements") contained as impurities in the copper-based alloy described under any of paragraphs (e) - (g), suppresses the action of enhancing blanking die wear resistance by the added carbon when the total content of one or two or more elements of the carbide-forming elements is equal to or more than 0.01 weight %. Therefore, the total content of the carbide-forming elements should preferably be limited to less than 0.01 weight %.

The present invention is based upon the above findings, and is characterized by:

(11) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, 0.0005 to 0.02 weight % of C, and the balance of Cu and inevitable impurities;

(12) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, 0.001 to 0.02 weight % of C, and the balance of Cu and inevitable impurities; and

(13) A copper-based alloy mentioned under paragraph (11) or (12) having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, with the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V, and Mo being limited to less than 0.01 weight %.

The resin adhesion of the above mentioned copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, containing 0.0005 to 0.02 weight % of C, is improved when one element selected from the group consisting of Al, Be, Ca, Cr, Mg and Si is added in an amount of 0.0007 to 0.5 weight % of Al, 0.0007 to 0.5 weight % of Ca, 0.0007 to 0.5 weight % of Be, 0.0007 to 0.5 weight % of Cr, 0.0007 to 0.5 weight % of Mg, or 0.0007 to 0.5 weight % of Si. Alternatively, two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si may be added in a total amount of 0.0007 weight % to 0.5 weight %. Among the group of Al, Be, Ca, Cr, Mg and Si, it is more preferable to add Mg and Si. Either Mg or Si may be added in an amount of 0.0007 weight % to 0.5 weight % of Mg or 0.0007 weight % to 0.5 weight % of Si, or both Mg and Si may be added in amounts of 0.0007 weight % to 0.5 weight % of Mg and 0.0007 weight % to 0.5 weight % of Si so that they coexist in the alloy.

Therefore, this invention is characterized by:

(14) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si in a total amount of 0.0007 to 0.5 weight %, and the balance being Cu and inevitable impurities;

(15) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and the balance being Cu and inevitable impurities;

(16) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Si and the balance being Cu and inevitable impurities;

(17) A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and 0.0007 to 0.5 weight % of Si, and the balance being Cu and inevitable impurities;

(18) A copper-based alloy mentioned under any of paragraphs (14), (15), (16) and (17) having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, in which C is contained in an amount of 0.001 to 0.02 weight %; and

(19) A copper-based alloy mentioned under any of paragraphs (14), (15), (16), (17) and (18) having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, in which the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.

The copper-based alloys described under paragraphs (11), (12), (13), (14), (15), (16), (17), (18) and (19), are intended to be used in the form of sheets.

Therefore, this invention is characterized by:

(20) A copper-based alloy sheet formed of a copper-based alloy described under any of paragraphs (11), (12), (13), (14), (15), (16), (17), (18) and (19).

Brief Description of the Drawing

[0019]

5 Fig. 1 is a perspective view showing a test piece.

Best Mode for Carrying Out the Invention

10 [0020] To manufacture the copper-based alloy and the sheet thereof having excellent blanking die wear resistance and resin adhesion strength, and the copper-based alloy and the sheet thereof having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, and the copper-based alloy and the sheet thereof having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, as well as excellent resin adhesion, according to the present invention, raw materials are prepared, which include highly pure electrolytic copper, iron-based alloy or copper-based alloy containing a reduced amount of carbide-forming elements, Cu-Zn mother alloy, Cu-Ni mother alloy, Cu-Sn mother alloy, Fe-C mother alloy, Cu-P mother alloy, Cu-Al mother alloy, Cu-Be mother alloy, Cu-Ca mother alloy, Cu-Cr mother alloy, Cu-Mg mother alloy, and Cu-Si mother alloy. First, the highly pure electrolytic copper is melted in an induction type smelting furnace using a crucible formed of graphite under a reducing atmosphere with the molten alloy meniscus being covered with a graphite solid, to obtain a molten alloy. The Cu and other elements-containing mother alloys are then added to obtain molten alloys according to test pieces, and finally the Fe-C mother alloy is added so as to adjust the composition. Then, the resulting molten alloys are cast by a semi-continuous casting method using a graphite mold, to form copper-based alloy ingots. These ingots are annealed at a temperature of 750 - 980 °C in a reducing atmosphere, and then are hot rolled, followed by being quenched and then scalped. Further, the ingots are repeatedly alternately cold rolled at a reduction ratio of 40 to 80 % and process-annealed at a temperature of 400 - 650 °C. Then, the ingots are subjected to final cold rolling, followed by stress relieving annealing at a temperature of 250 - 350 °C, and other treatments, to obtain sheets.

25 [0021] The chemical compositions of the copper-based alloy of the present invention having excellent blanking die wear resistance, and the copper-based alloy of the present invention having excellent blanking die wear resistance as well as excellent resin adhesion have been limited as stated above, for the following reasons:

30 Fe :

[0022] The Fe component is solid solved in the Cu matrix and forms a compound with P, to increase the strength and hardness of the alloy. However, if the Fe content is less than 1.5 weight %, the above effects cannot be achieved to a desired extent, whereas, if the Fe content exceeds 2.4 weight %, the alloy has drastically degraded platability due to surface discontinuity, and further, decreases in both electrical conductivity and workability. Therefore, the Fe content has been limited to the range of 1.5 to 2.4 weight %, and preferably to a range of 1.8 to 2.3 weight %.

P :

40 [0023] The P component has a deoxidation effect and also acts to improve the strength of the alloy by forming a compound with Fe. However, if the P content is less than 0.008 weight %, the above effects cannot be achieved to a desired extent, whereas, if the P content exceeds 0.08 weight %, the alloy decreases in both electrical conductivity and workability. Therefore, the P content has been limited to the range of 0.008 to 0.08 weight %, and preferably to a range of 0.01 to 0.05 weight %.

45 Zn :

[0024] The Zn component is solid solved in the Cu matrix to increase the soldering thermal peeling resistance of the alloy. However, if the Zn content is less than 0.01 weight %, the above effect cannot be achieved to a desired extent. On the other hand, if the Zn content exceeds 0.50 weight %, the above effect is saturated. Therefore, the Zn content has been limited to the range of 0.01 to 0.50 weight %, and preferably to a range of 0.05 to 0.35 weight %.

C :

55 [0025] The C component is an element which is extremely difficult to solid solve in copper. However, adding a very small amount of C refines the crystal grains of the cast ingot which restrains intergranular cracking during hot rolling, and further, improves blanking die wear resistance. However, if the C content is less than 0.0005 weight %, the above effects cannot be achieved to a desired extent, whereas, if the C content exceeds 0.02 weight %, intergranular cracking

undesirably occurs during hot rolling. Therefore, the C content has been limited to the range of 0.0005 to 0.02 weight %. Preferably, the C content should be limited to a range of 0.001 to 0.02 weight %, and more preferably to a range of 0.001 to 0.008 weight %

5 Ni :

[0026] The Ni component is solid solved in the Cu matrix to strengthen and improve the fatigue resistance to lead bending (repeated bending fatigue resistance) of the same. However, if the Ni content is less than 0.003 weight %, the above effects cannot be achieved to a desired extent, whereas, if the Ni content exceeds 0.5 weight %, the alloy drastically decreases in electrical conductivity. Therefore, the Ni content has been limited to the range of 0.003 to 0.5 weight %, and preferably to a range of 0.008 to 0.2 weight %.

Sn :

[0027] The Sn component is solid solved in the Cu matrix to increase the strength and improve the solderability. However, if the Sn content is less than 0.003 weight %, the above effects cannot be achieved to a desired extent, whereas, if the Sn content exceeds 0.5 weight %, the alloy drastically decreases in electrical conductivity. Therefore, the Sn content has been limited to the range of 0.003 to 0.5 weight %, and preferably to a range of 0.008 to 0.2 weight %.

Al, Be, Ca, Cr, Mg and Si :

[0028] These components may be contained in the copper-based alloy if required, because they each have a deoxidation effect as well as an effect to suppress the exhaustion of C by forming an antioxidant film on the molten alloy meniscus. Further, these components act to improve the strength of the Fe-Zn-P alloy, as well as to improve the resin adhesion of the same. However, if the total content of one or two or more components of this group of Al, Be, Ca, Cr, Mg and Si is less than 0.0007 weight %, the above effects cannot be achieved to a desired extent, whereas, if the total content of the same exceeds 0.5 weight %, electrical conductivity decreases, and further, large oxides and precipitates easily become formed and the surface cleanness is lost. Therefore, the content of these components has been limited to the range of 0.0007 to 0.5 weight %, and preferably to a range of 0.005 to 0.15 weight %. Among these components, Mg and Si are most preferable, Be is the next most preferable, and Al, Ca and Cr are preferable next to Be.

Carbide-forming elements (Nb, Ti, Zr, Ta, Hf, W, V and Mo) :

[0029] These components easily react to form carbides. Therefore, unless these components are restricted in their total content, they will react with the C in the molten alloy to form hard carbides, resulting in a decrease in the action of C to enhance the blanking die wear resistance. Therefore, the total content of one or two or more elements of the carbide-forming elements has been limited to less than 0.01 weight %, and preferably to less than 0.001 weight %. The Mn, Co, and Ag components, and the Sb, Bi and Pb components may be added to a maximum of 0.5 weight % and 0.3 weight % respectively, without spoiling the gist of the present invention.

Examples

Example 1

[0030] As raw materials, highly pure electrolytic copper, iron-based alloy or copper-based alloy containing carbide-forming elements, Cu-Zn mother alloy, Cu-P mother alloy, Fe-C mother alloy and pure iron were prepared. First, the highly pure electrolytic copper, iron-based alloy or copper-based alloy containing carbide-forming elements and pure iron were melted in a CO + N₂ gaseous atmosphere in a coreless induction smelting furnace using a crucible formed of graphite, with the molten alloy meniscus being covered with a graphite solid, to obtain a molten alloy. Next, the Cu-P mother alloy was added to the obtained molten alloy for deoxidation, then the Cu-Zn mother alloy, and lastly, the Fe-C mother alloy were added so as to adjust the composition. Then, the resulting molten alloys were cast using a graphite nozzle and a graphite mold, into ingots, each having a size of 160mm in thickness, 450mm in width, and 1600mm in length, to obtain ingots having chemical compositions shown in Tables 1 to 3, as copper-based alloys Nos. 1 to 16 according to the present invention, comparative copper-based alloys Nos. 1 to 3 and a conventional copper-based alloy No. 1.

[0031] These ingots of the copper-based alloys Nos. 1 to 16 according to the present invention, comparative copper-based alloys Nos. 1 to 3 and conventional copper-based alloy No. 1 were hot-rolled at a temperature of 860°C into

hot-rolled plates each having a thickness of 11mm. Then, the plates were quenched, followed by each having its upper and lower side surfaces scalped by 0.5mm per each surface and its opposite lateral side surfaces scalped by 3mm per each surface, into a thickness of 10mm. The plates were then cold-rolled at a reduction ratio of 84% into cold-rolled sheets having a thickness of 1.60mm. Then, the sheets were process-annealed at 530°C for 1 hour and cold-rolled at a reduction ratio of 69% into cold-rolled sheets having a thickness of 0.50mm. The sheets were then again process-annealed at a temperature within a range of 460 ~ 500°C for 1 hour. After acid pickling, the sheets were cold-rolled at a reduction ratio of 50% into cold-rolled sheets having a thickness of 0.25mm. Finally, the sheets were annealed at 300°C for 2 minutes for stress relief. Thus copper-based alloy sheet strips of the copper-based alloys Nos. 1 to 16 according to the present invention, comparative copper-based alloys Nos. 1 to 3 and conventional copper-based alloy No. 1 were prepared.

[0032] These prepared copper-based alloy sheet strips of the copper-based alloys Nos. 1 to 16 according to the present invention, comparative copper-based alloys Nos. 1 to 3 and conventional copper-based alloy No. 1, were blanked under the following conditions:

[0033] A compact dieing machine (Model LEM 3201, manufactured by Noritsu Kikai) with a commercially available blanking die formed of a WC-based hard alloy having a composition of 16 weight % of Co, and the balance of WC was used to carry out continuous blanking to obtain one million blanked circular chips with a diameter of 5mm, from the Cu alloy sheet strips having a size of 0.25mm in thickness and 25mm in width. 20 bores obtained immediately after the start of the blanking and 20 bores obtained immediately before the termination of the same were selected, and the diameter of each bore was measured. An amount of change in the diameter was determined from two average diameter values of the respective groups of 20 bores, to adopt it as the amount of wear of the blanking die. The amount of wear of the blanking die by the conventional copper-based alloy No. 1 in Table 3 was set as a reference value of 1, and the wear amounts by the other copper-based alloys were converted into values relative to the reference value, as shown in Tables 1 to 3, to thereby evaluate the blanking die wear resistance.

TABLE 1

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)						WEAR AMOUNT OF MOLD (RELATIVE RATIO)	REMARKS
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENTS			
COPPER-BASED ALLOYS OF PRESENT INVENTION	1	1.57	0.032	0.153	0.008	BELOW 0.001	0.66	-
	2	1.92	0.025	0.104	0.010	BELOW 0.001	0.61	-
	3	1.89	0.023	0.122	0.005	BELOW 0.001	0.72	-
	4	2.13	0.028	0.089	0.002	BELOW 0.001	0.77	-
	5	2.12	0.037	0.093	0.003	BELOW 0.001	0.75	-
	6	2.08	0.031	0.133	0.008	BELOW 0.001	0.68	-
	7	2.14	0.033	0.147	0.009	0.003	0.79	-
	8	2.13	0.026	0.155	0.007	BELOW 0.001	0.69	-

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 2

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)						WEAR AMOUNT OF MOLD (RELATIVE RATIO)	REMARKS
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENT			
9	2.42	0.032	0.152	0.001	0.002		0.85	-
10	2.38	0.025	0.107	0.0006	BELOW 0.001		0.85	-
11	2.16	0.025	0.124	0.006	BELOW 0.001		0.70	-
12	2.15	0.031	0.266	0.010	BELOW 0.001		0.63	-
13	2.13	0.033	0.023	0.008	0.007		0.84	-
14	2.14	0.041	0.133	0.014	BELOW 0.001		0.56	-
15	2.09	0.062	0.451	0.019	BELOW 0.001		0.52	-
16	2.10	0.080	0.353	0.0008	BELOW 0.001		0.84	-

COPPER-BASED ALLOYS OF PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 3

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)					WEAR AMOUNT OF MOLD (RELATIVE RATIO)	REMARKS
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENTS		
1	2.14	0.033	0.121	* 0.0003	BELOW 0.001	0.98	-
2	2.11	0.027	0.150	* 0.0020	BELOW 0.001	0.52	INTERGRANULAR CRACK WHEN HOT ROLLED
3	2.14	0.035	0.136	0.006	* 0.012	1.13	-
CONVENTIONAL COPPER-BASED ALLOY 1	2.19	0.026	0.108	-	-	-	-

* INDICATES VALUES OUTSIDE THE RANGE OF THE PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

[0034] The results in Tables 1 to 3 show that the sheets of the present invention copper-based alloys Nos. 1 to 16 all exhibit more excellent blanking die wear resistance compared with the sheet of the conventional copper-based alloy No. 1. The results also show that the comparative copper-based alloy No. 1, containing less than 0.0005 weight % of

C, and comparative copper-based alloy No. 3, containing totally 0.01 or more weight % of the carbide-forming elements both exhibit insufficient blanking die wear resistance. Further, comparative copper-based alloy No. 2 which contain more than 0.02 weight % of C exhibits intergranular cracking during the hot-rolling process and is therefore not preferable.

Example 2

[0035] Molten alloys with almost desired Fe, P, Zn compositions were prepared in a manner similar to that of Example 1. Then, one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si was/were added in the toxin of a mother alloy(s) with Cu, to form an antioxidant film on the molten alloy meniscus. Then, an Fe-C mother alloy was added, to obtain the copper-based alloys having chemical compositions shown in Tables 4 to 7 as copper-based alloys Nos. 17 to 38 according to the present invention, comparative copper-based alloys Nos. 4 to 6 and conventional copper-based alloy No. 2. Under the same conditions as Example 1, the copper-based alloys were cold-rolled into a thickness of 0.25mm, and finally annealed for stress relief at a temperature of 300 °C for 2 minutes, to prepare sheet strips of the copper-based alloys Nos. 17 to 38 according to the present invention, comparative copper-based alloys Nos. 4 to 6 and conventional copper-based alloys No. 2.

[0036] The blanking die wear resistance by these sheet strips was evaluated by the same method as adopted in Example 1, with the amount of die wear by the conventional copper-based alloy No. 2 in Table 8 set as a reference value of 1, and relative values thereto are shown in Tables 8 and 9.

[0037] Next, the sheet strips of the copper-based alloys Nos. 17 to 38 according to the present invention, comparative copper-based alloys Nos. 4 to 6 and conventional copper-based alloy No. 2 were cut into alloy test piece sheets 1, each having a size of 25mm x 150mm, as shown in Fig. 1.

[0038] Six truncated cone-shaped epoxy resin pieces 2 (Model EME-6300H, manufactured by Sumitomo Bakelite Co., Ltd.) each having a stud 3 were molding-bonded to an upper surface of each alloy test piece sheet 1 at a bonding surface of 1.0cm², then soaked for 8 hours at a temperature of 175°C for curing, to prepare a test piece. The studs 3 on the test piece sheet were pulled with a tension tester to measure the adhesion strength of the alloy test piece sheet 1 and the epoxy resin pieces 2. Average values of the measurement results are shown in Tables 8 and 9, based upon which the resin adhesion of the sheet strips of the copper-based alloys Nos. 17 to 38 according to the present invention, comparative copper-based alloys Nos. 4 to 6 and conventional copper-based alloy No. 2 were evaluated.

TABLE 4

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)					
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENTS	Al, Be, Ca, Cr, Mg, Si
17	2.14	0.035	0.087	0.002	BELOW 0.001	Mg : 0.0010
18	2.12	0.033	0.096	0.003	BELOW 0.001	Mg : 0.015
19	2.21	0.027	0.132	0.013	BELOW 0.001	Mg : 0.042
20	2.10	0.031	0.144	0.019	BELOW 0.001	Mg : 0.076
21	2.17	0.026	0.156	0.007	BELOW 0.001	Mg : 0.113
22	1.62	0.03	0.152	0.005	BELOW 0.001	Si : 0.0022
23	1.97	0.031	0.125	0.001	BELOW 0.001	Si : 0.121
24	2.01	0.024	0.121	0.014	BELOW 0.001	Si : 0.036

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 5

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : CU AND INEVITABLE IMPURITIES)						
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENTS	Al, Be, Ca, Cr, Mg, Si	
25	2.15	0.031	0.085	0.002	BELOW 0.001	Si : 0.0008	
26	2.15	0.026	0.093	0.003	BELOW 0.001	Mg : 0.022, Si : 0.023	
27	2.17	0.035	0.144	0.008	BELOW 0.001	Mg : 0.042, Si : 0.131	
28	2.22	0.033	0.154	0.016	BELOW 0.001	Mg : 0.076, Si : 0.045	
29	2.15	0.026	0.152	0.007	BELOW 0.001	Mg : 0.113, Si : 0.009	
30	1.61	0.033	0.152	0.005	BELOW 0.001	Be : 0.089	
31	1.57	0.030	0.154	0.0006	BELOW 0.001	Al : 0.089	
32	1.90	0.025	0.125	0.005	BELOW 0.001	Ca : 0.015	

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 6

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)					
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENTS	Al, Be, Ca, Cr, Mg, Si
33	2.23	0.033	0.088	0.002	BELOW 0.001	Cr : 0.0011
34	2.13	0.036	0.091	0.006	BELOW 0.001	Mg : 0.015, Si : 0.079, Al : 0.042
35	2.17	0.035	0.144	0.017	BELOW 0.001	Mg : 0.076, Si : 0.045, Be : 0.021, Ca : 0.006,
36	2.20	0.031	0.093	0.005	BELOW 0.001	Cr : 0.018, Al : 0.019
37	2.16	0.034	0.083	0.002	BELOW 0.001	Cr : 0.008, Al : 0.021, Si : 0.023, Ca : 0.009, Be : 0.006, Mg : 0.023,
38	1.94	0.022	0.125	0.005	BELOW 0.001	Si : 0.008, Al : 0.021, Mg : 0.023, Ca : 0.014,

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 7

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)						
	Fe	P	Zn	C	※CARBIDE-FORMING ELEMENTS	Al, Be, Ca, Cr, Mg, Si	
COMPARATIVE COPPER-BASED ALLOYS	4	2.13	0.035	0.126	* 0.0003	BELOW 0.001	Mg : 0.021, Si : 0.025,
	5	2.12	0.026	0.157	* 0.022	BELOW 0.001	Mg : 0.023, Si : 0.022,
	6	2.14	0.032	0.136	0.006	* 0.013	Mg : 0.021, Si : 0.023,
CONVENTIONAL COPPER-BASED ALLOY 2	2.17	0.027	0.10	-	-	-	

* INDICATES VALUES OUTSIDE THE RANGE OF THE PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 8

SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS	SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS
17	0.77	530	-	25	0.77	535	-
18	0.76	560	-	26	0.77	610	-
19	0.60	565	-	27	0.74	630	-
20	0.56	570	-	28	0.59	570	-
21	0.74	620	-	29	0.74	625	-
22	0.74	540	-	30	0.74	615	-
23	0.82	630	-	31	0.86	620	-
24	0.60	570	-	32	0.72	550	-

TABLE 9

SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS	SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS
33	0.77	525	-	4	0.99	615	-
34	0.74	625	-	5	0.54	550	INTERGRANULAR CRACK WHEN HOT ROLLED
35	0.59	575	-	6	1.15	620	-
36	0.71	590	-	CONVENTIONAL COPPER-BASED ALLOY 2			
37	0.81	620	-				
38	0.73	615	-				

[0039] The results in Tables 4 to 9 show that the sheet strips of the present invention copper-based alloys Nos. 17 to 38, which contain 0.0005 - 0.02 weight % of C, and further totally contains 0.0007 - 0.5 weight % of one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si, exhibit superior blanking die wear resist-

ance and resin adhesion compared with the sheet strip of the conventional copper-based alloy No. 2. The results also show that the comparative copper-based alloy No. 4, containing less than 0.0005 weight % of C, and comparative copper-based alloy No. 6, containing 0.01 or more weight % of carbide-forming elements, both exhibit insufficient blanking die wear resistance. Further, comparative copper-based alloy No. 5 which contains more than 0.02 weight % of C exhibits intergranular cracking during the hot-rolling process and is therefore not preferable.

Example 3

[0040] As raw materials, highly pure electrolytic copper, iron-based alloy or copper-based alloy containing carbide-forming elements, Cu-Zn mother alloy, Cu-P mother alloy, Cu-Ni mother alloy, Cu-Sn mother alloy, Fe-C mother alloy and pure iron were prepared. First, the highly pure electrolytic copper, iron-based alloy or copper-based alloy containing carbide-forming elements, Cu-Ni mother alloy, Cu-Sn mother alloy and pure iron were melted in a CO + N₂ gaseous atmosphere in a coreless induction smelting furnace using a crucible formed of graphite, with the molten alloy being covered with a graphite solid, to obtain a molten alloy. Next, the Cu-P mother alloy was added to the obtained molten alloy for deoxidation, then the Cu-Zn mother alloy, and lastly, the Fe-C mother alloy were added so as to adjust the composition. Then, the resulting molten alloys were cast using a graphite nozzle and a graphite mold, into ingots, each having a size of 160mm in thickness, 450mm in width, and 1600mm in length, to obtain ingots having chemical compositions shown in Tables 10 to 12, as copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3.

[0041] These ingots of the copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3 were hot-rolled at a temperature of 860°C into hot-rolled plates each having a thickness of 11mm. Then, the plates were quenched, followed by each having its upper and lower side surfaces scalped by 0.5mm per each surface and its opposite lateral side surfaces scalped by 3mm per each surface, into a thickness of 10mm. The plates were then cold-rolled at a reduction ratio of 84% into cold-rolled sheets having a thickness of 1.60mm. Then, the sheets were process-annealed at 530°C for 1 hour and cold-rolled at a reduction ratio of 80% into cold-rolled sheets having a thickness of 0.32mm. The sheets were then again process-annealed at a temperature of 480°C for 1 hour. After acid pickling, the sheets were cold-rolled at a reduction ratio of 53% into cold-rolled sheets having a thickness of 0.15mm. Finally, the sheets were annealed at 300°C for 2 minutes for stress relief. Thus, sheet strips of the copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3 were prepared.

[0042] These prepared copper-based alloy sheet strips of the copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3, were subjected to the following tests, and the results of the tests are shown in Tables 13 and 14.

(A) Blanking Die Wear Test

[0043] A compact dieing machine (Model LEM 3201, manufactured by Noritsu Kikai) with a commercially available blanking die formed of a WC-based hard alloy having a composition of 16 weight % of Co, and the balance of WC was used to carry out continuous blanking to obtain one million blanked circular chips with a diameter of 5mm, from the Cu alloy sheet strips of the copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3, having a size of 0.15mm in thickness and 25mm in width. 20 bores obtained immediately after the start of the blanking and 20 bores obtained immediately before the termination of the same were selected, and the diameter of each bore was measured. An amount of change in the diameter was determined from two average diameter values of the respective groups of 20 bores, to adopt it as the amount of wear of the blanking die. The amount of wear of the blanking die by the conventional copper-based alloy No. 3 in Table 12 was set as a reference value of 1, and the wear amounts by the other copper-based alloys were converted into values relative to the reference value, as shown in Tables 13 and 14, to thereby evaluate the blanking die wear resistance.

(B) Repeated Bending Test (according to MIL-STD-883/2004)

[0044] Sheets of the copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3, each having a size of 0.15mm in thickness, 25mm in width, and 300mm in length, were blanked into test pieces each having an increased width portion of a size of 1.5mm in width and 6mm in length, and a reduced width portion of a size of 0.5mm in width and 10mm in length. The increased width portion of each test piece was fixed to a lead fatigue tester (manufactured by Hybrid Machine Products Co.), and the reduced width portion was loaded with an 8oz. (226.8g) weight. The reduced width portion of the test piece was bent by 90 degrees in one direction (first bending), then bent back by 90 degrees in the opposite direction into the orig-

inal position (second bending), the first and second bendings being counted as one. The above bending operations were repeated until the test piece ruptured, and the number of bending before the rupture was counted. Five test pieces were cut out from the sheet of the copper-based alloy in a direction parallel with the rolling direction, and further five test pieces cut out from the sheet in a direction perpendicular to the rolling direction, per each copper-based alloy. An average value of the number of bending before the rupture was calculated for all the test pieces, and the results are shown in Tables 13 and 14, to thereby evaluate the repeated bending fatigue resistance.

(C) Solderability Test

[0045] The solderability was tested with MODEL WET-6000 manufactured by Rhesca Co., Ltd, using the meniscograph method. More specifically, test pieces each having a size of 0.15mm in thickness, 10mm in width, and 50mm in length, were cut out from the copper-based alloys Nos. 39 to 54 according to the present invention, comparative copper-based alloys Nos. 7 to 11 and conventional copper-based alloy No. 3. The test pieces were polished with a #1000 emery paper, and then degreased with acetone. Then, the test pieces were acid pickled with an 10% aqueous sulfuric acid solution at 40°C for 1 minute, followed by washing and drying, and then coated with a low-activated rosin flux. The test pieces coated with the low-activated rosin flux were then dipped in a bath of a 60 weight % Sn - 40 weight % Pb solder held at a temperature of 230°C, under conditions of dipping depth: 2mm, dipping speed: 16mm/sec, and sensitivity: 5g. Time t was measured, that elapses from the start of dipping when buoyancy starts acting upon the test piece to the time the buoyancy becomes zero after reaching a peak value. The measurement results are shown in Tables 13 and 14. The solderability was evaluated by the value t , such that the smaller the value t , the better the wettability with respect to the solder.

TABLE 10

CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)							
SPECIMEN	Fe	P	Zn	Ni	Sn	C	※CARBIDE-FORMING ELEMENTS
	39	1.59	0.030	0.155	0.268	0.052	0.007
40	1.90	0.025	0.113	0.452	0.003	0.001	BELOW 0.001
41	1.92	0.026	0.122	0.004	0.460	0.006	BELOW 0.001
42	2.15	0.031	0.085	0.035	0.038	0.002	BELOW 0.001
43	2.11	0.033	0.091	0.003	0.036	0.004	BELOW 0.001
44	2.05	0.031	0.133	0.012	0.044	0.007	BELOW 0.001
45	2.13	0.033	0.157	0.026	0.045	0.009	0.003
46	2.10	0.028	0.151	0.094	0.035	0.008	BELOW 0.001

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

COPPER-BASED ALLOYS OF PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 12

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : CU AND INEVITABLE IMPURITIES)						
	Fe	P	Zn	Ni	Sn	C	※CARBIDE-FORMING ELEMENTS
COMPARATIVE COPPER-BASED ALLOYS	7	2.14	0.031	0.131	0.052	0.048	* 0.0003
	8	2.12	0.025	0.141	0.024	* 0.002	* 0.023
	9	2.13	0.035	0.132	* 0.002	0.055	* 0.013
	10	2.11	0.027	0.150	* 0.022	0.043	BELOW 0.001
	11	2.16	0.035	0.136	0.047	* 0.635	BELOW 0.001
CONVENTIONAL COPPER-BASED ALLOY 3	2.17	0.031	0.130	-	-	-	BELOW 0.001

* INDICATES VALUES OUTSIDE THE RANGE OF THE PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 13

SPECIMEN		WEAR AMOUNT OF MOLD (RELATIVE RATIO)	NUMBER OF REPEATED BENDING (No.)	t (Sec)	REMARKS
COPPER-BASED ALLOYS OF PRESENT INVENTION	39	0.70	6.0	0.8	-
	40	0.81	6.4	0.9	-
	41	0.71	5.2	0.6	-
	42	0.78	5.5	0.7	-
	43	0.74	5.1	0.8	-
	44	0.69	5.3	0.8	-
	45	0.80	5.3	0.8	-
	46	0.68	5.8	0.8	-
	47	0.87	6.3	0.8	-
	48	0.85	5.4	0.9	-
	49	0.69	5.5	0.8	-
	50	0.60	5.3	0.9	-

TABLE 14

SPECIMEN		WEAR AMOUNT OF MOLD (RELATIVE RATIO)	NUMBER OF REPEATED BENDING (No.)	t (Sec)	REMARKS
COPPER-BASED ALLOYS OF PRESENT INVENTION	51	0.84	5.6	0.8	-
	52	0.58	5.3	0.9	-
	53	0.51	5.1	0.8	-
	54	0.84	5.6	0.7	-
COMPARATIVE COPPER-BASED ALLOYS	7	0.98	5.6	0.8	-
	8	0.51	5.1	1.4	CRACK WHEN HOT ROLLED
	9	1.15	4.6	0.8	-
	10	0.86	6.5	0.8	DECREASE IN ELECTRICAL CONDUCTIVITY
	11	0.69	5.6	0.6	DECREASE IN ELECTRICAL CONDUCTIVITY
CONVENTIONAL COPPER-BASED ALLOY 3		1	4.5	1.2	-

[0046] The results in Tables 10 to 14 show that the sheets of the present invention copper-based alloys Nos. 39 to 54 all exhibit superiority in blanking die wear resistance, repeated bending fatigue resistance, and solderability to the sheet of the conventional copper-based alloy No. 3. The results also show that the comparative copper-based alloy No. 7, containing less than 0.0005 weight % of C, and comparative copper-based alloy No. 9, containing totally 0.01 or more weight % of the carbide-forming elements, both exhibit insufficient blanking die wear resistance. Further, comparative copper-based alloy No. 8 which contains more than 0.02 weight % of C exhibits intergranular cracking during the hot-rolling process and is therefore not preferable, and addition of more than 0.5 weight % of Ni and more than 0.5 weight % of Sn reduces electrical conductivity and is therefore not preferable.

Example 4

[0047] Molten alloys were prepared with addition of Fe, P, Zn, Ni and Sn in a manner similar to that in Example 3. Then, one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si was/were added to form an antioxidant film on the molten alloy meniscus. Lastly, an Fe-C mother alloy was added so as to adjust the contents of C and Fe to obtain copper-based alloys having chemical compositions shown in Tables 15 to 18, as copper-based alloys Nos. 55 to 76 according to the present invention, comparative copper-based alloys Nos. 12 to 16 and conventional copper-based alloy No. 4. Under the same conditions as in Example 3, the copper-based alloys were cold-rolled into cold-rolled sheets having a thickness of 0.15mm, and finally annealed for stress relief at a temperature of 300 °C for 2 minutes, to prepare sheet strips of the copper-based alloys Nos. 55 to 76 according to the present invention,

comparative copper-based alloys Nos. 12 to 16 and conventional copper-based alloy No. 4.

[0048] A blanking die wear resistance test was conducted on these sheet strips using the same method as adopted in Example 3, with the amount of die wear by the conventional copper based alloy No. 4 set as a reference value of 1, and relative values thereto are shown in Tables 19 to 22, to thereby evaluate the blanking die wear resistance. Further, a repeated bending fatigue resistance test was conducted using the same method as adopted in Example 3, to measure the number of times each test piece was bent before rupture occurred, and the measurement results are shown in Tables 19 to 22, to thereby evaluate the repeated bending fatigue resistance. Further, a solderability test was conducted using the same method as adopted in Example 1 to determine the value t , which is also shown in Tables 19 to 22. The solderability was evaluated by the value t , such that the smaller the value t , the better the wettability with respect to the solder.

(D) Resin Adhesion Test

[0049] Next, the sheet strips of the copper-based alloys Nos. 55 to 76 according to the present invention, comparative copper-based alloys Nos. 12 to 16 and conventional copper-based alloy No. 4 were cut into alloy test piece sheets 1, each having a size of 25mm x 150mm, as shown in Fig. 1.

[0050] Six truncated cone-shaped epoxy resin pieces 2 (Model EME-6300H, manufactured by Sumitomo Bakelite Co., Ltd) each having a stud 3 were molding-bonded to an upper surface of each alloy test piece sheet 1 at a bonding surface of 1.0cm^2 , then soaked for 8 hours at a temperature of 175°C for curing, to prepare a test piece. The studs 3 on the test piece were pulled with a tension tester to measure the adhesion strength of the alloy test piece sheet 1 and the epoxy resin pieces 2. Average values of the measurement results are shown in Tables 19 to 22, based upon which the resin adhesion of the sheet strips of the copper-based alloys Nos. 55 to 76 according to the present invention, comparative copper-based alloys Nos. 12 to 16 and conventional copper-based alloy No. 4 were evaluated.

TABLE 15

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)								
	Fe	P	Zn	Ni	Sn	C	※CARBIDE-FORMING ELEMENTS	REMARKS	
COPPER-BASED ALLOYS OF PRESENT INVENTION	55	2.18	0.032	0.097	0.004	0.028	0.002	BELOW 0.001	Mg : 0.0011
	56	2.22	0.033	0.090	0.335	0.051	0.004	BELOW 0.001	Mg : 0.014
	57	2.20	0.021	0.125	0.036	0.037	0.012	BELOW 0.001	Mg : 0.040
	58	2.14	0.032	0.141	0.038	0.068	0.018	BELOW 0.001	Mg : 0.082
	59	2.17	0.024	0.150	0.045	0.340	0.008	BELOW 0.001	Mg : 0.117
	60	1.64	0.030	0.147	0.006	0.026	0.005	BELOW 0.001	Si : 0.0020
	61	2.03	0.036	0.122	0.259	0.033	0.001	BELOW 0.001	Si : 0.125
	62	2.11	0.027	0.124	0.041	0.038	0.013	BELOW 0.001	Si : 0.031

COPPER-BASED ALLOYS OF PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 16

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : CU AND INEVITABLE IMPURITIES)							
	Fe	P	Zn	Ni	Sn	C	※CARBIDE-FORMING ELEMENTS	REMARKS
63	2.17	0.033	0.081	0.037	0.005	0.003	BELOW 0.001	Si : 0.0008
64	2.14	0.022	0.096	0.006	0.330	0.004	BELOW 0.001	Mg : 0.020, Si : 0.022
65	2.21	0.032	0.131	0.038	0.035	0.007	BELOW 0.001	Mg : 0.038, Si : 0.035
66	2.22	0.030	0.155	0.055	0.052	0.014	BELOW 0.001	Mg : 0.074, Si : 0.113
67	2.18	0.026	0.150	0.355	0.005	0.007	BELOW 0.001	Mg : 0.110, Si : 0.009
68	1.63	0.031	0.152	0.032	0.036	0.004	BELOW 0.001	Be : 0.075
69	1.58	0.033	0.146	0.038	0.029	0.001	BELOW 0.001	Al : 0.085
70	1.95	0.028	0.128	0.041	0.037	0.006	BELOW 0.001	Ca : 0.013

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 17

SPECIMEN	CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : Cu AND INEVITABLE IMPURITIES)							
	Fe	P	Zn	Ni	Sn	C	※CARBIDE-FORMING ELEMENTS	REMARKS
71	2.24	0.035	0.084	0.045	0.044	0.002	BELOW 0.001	Cr : 0.0003
72	2.22	0.036	0.095	0.037	0.028	0.005	BELOW 0.001	Mg : 0.014, Al : 0.036, Si : 0.071
73	2.17	0.032	0.146	0.056	0.047	0.016	BELOW 0.001	Mg : 0.072, Be : 0.020, Ca : 0.006
74	2.24	0.033	0.090	0.033	0.035	0.004	BELOW 0.001	Cr : 0.016, Al : 0.015
75	2.15	0.028	0.086	0.041	0.039	0.002	BELOW 0.001	Ca : 0.007, Si : 0.023, Be : 0.006, Mg : 0.0021
76	1.94	0.025	0.122	0.035	0.054	0.005	BELOW 0.001	Si : 0.009, Mg : 0.025, Ca : 0.010

COPPER-BASED ALLOYS OF PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 18

CHEMICAL COMPOSITION (WEIGHT %) (BALANCE : CU AND INEVITABLE IMPURITIES)								
SPECIMEN	Fe	P	Zn	Ni	Sn	C	※CARBIDE-FORMING ELEMENTS	REMARKS
	12	2.15	0.032	0.122	0.043	0.035	* 0.0003	BELOW 0.001 Mg : 0.022, Si : 0.027
13	2.18	0.024	0.148	0.036	* 0.002	* 0.024	BELOW 0.001 Mg : 0.020, Si : 0.022	
14	2.14	0.035	0.131	* 0.001	0.039	0.007	* 0.013 Mg : 0.023	
15	2.18	0.025	0.151	* 0.634	0.047	0.005	BELOW 0.001 Mg : 0.021	
16	2.14	0.032	0.141	0.033	* 0.618	0.007	BELOW 0.001 Si : 0.022	
CONVENTIONAL COPPER-BASED ALLOY 4	2.25	0.031	0.122	-	0.035	-	-	-

* INDICATES VALUES OUTSIDE THE RANGE OF THE PRESENT INVENTION

※ CARBIDE-FORMING ELEMENTS (Nb+Ti+Zr+Ta+Hf+W+V+Mo)

TABLE 19

SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	NUMBER OF REPEATED BENDING (No.)	t (Sec)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS
55	0.76	5.2	0.8	525	-
56	0.76	6.4	0.8	550	-
57	0.60	5.4	0.9	560	-
58	0.57	5.2	0.9	570	-
59	0.72	5.6	0.7	615	-
60	0.74	5.3	0.8	540	-
61	0.83	6.4	0.8	620	-
62	0.61	5.5	0.9	565	-

COPPER-BASED ALLOYS OF PRESENT INVENTION

TABLE 20

SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	NUMBER OF REPEATED BENDING (No.)	t (Sec)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS
63	0.76	5.4	0.9	530	-
64	0.76	5.4	0.6	610	-
65	0.75	5.5	0.8	570	-
66	0.60	5.5	0.9	630	-
67	0.76	6.4	0.9	620	-
68	0.75	5.7	0.8	610	-
69	0.86	5.6	0.8	615	-
70	0.71	5.3	0.8	550	-

COPPER-BASED ALLOYS OF PRESENT INVENTION

TABLE 21

SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	NUMBER OF REPEATED BENDING (No.)	t (Sec)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS
71	0.77	5.5	0.7	520	-
72	0.75	5.5	0.8	615	-
73	0.60	5.3	0.9	560	-
74	0.72	5.5	0.8	585	-
75	0.80	5.6	0.8	610	-
76	0.73	5.6	0.8	605	-

COPPER-BASED ALLOYS OF PRESENT INVENTION

TABLE 22

SPECIMEN	WEAR AMOUNT OF MOLD (RELATIVE RATIO)	NUMBER OF REPEATED BENDING (No.)	t (Sec)	RESIN ADHESION STRENGTH (N/cm ²)	REMARKS
12	0.98	5.5	0.7	610	-
13	0.56	5.1	1.4	550	CRACK WHEN HOT ROLLED
14	1.13	4.5	0.8	610	-
15	0.77	6.5	0.8	600	DECREASE IN ELECTRICAL CONDUCTIVITY
16	0.74	5.7	0.6	605	DECREASE IN ELECTRICAL CONDUCTIVITY
CONVENTIONAL COPPER-BASED ALLOY 4	1	4.5	0.8	405	-

[0051] The results in Tables 15 to 22 show that the sheet strips of the present invention copper-based alloys Nos. 55 to 76, which contain one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si, exhibit superiority in both blanking die wear resistance and repeated bending fatigue resistance as well as superiority in resin adhesion, to the sheet strip of the conventional copper-based alloy No. 4. The results also show that the com-

parative copper-based alloy No. 12, containing less than 0.0005 weight % of C, and one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si, and the comparative copper-based alloy No. 14, containing totally 0.01 or more weight % of the carbide-forming elements, both exhibit insufficient blanking die wear resistance. Further, the results show that the comparative copper-based alloy No. 13, which contains more than 0.02 weight % of C and less than 0.003 weight % of Sn, exhibits intergranular cracking during the hot-rolling process and thus is inferior in solderability. Further, the results show that electrical conductivity undesirably decreases when Ni is added in an amount exceeding 0.5 weight % and also when Sn is contained in an amount exceeding 0.5 weight %.

Industrial Application

[0052] As described above, the copper-based alloys of the present invention are superior in blanking die wear resistance, repeated bending fatigue resistance and solderability to the conventional copper-based alloy, and also superior in resin adhesion to the latter. Therefore, the copper-based alloy of the present invention can greatly contribute to the development of the electronic industry.

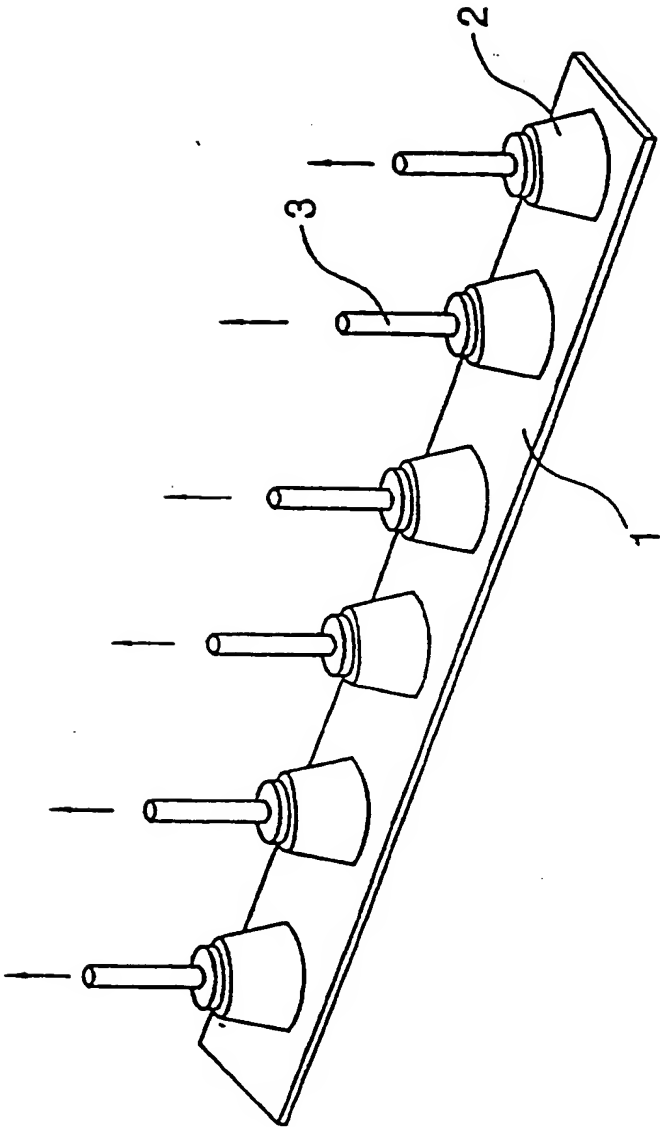
Claims

1. A copper-based alloy having excellent blanking die wear resistance, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, 0.0005 to 0.02 weight % of C, and the balance of Cu and inevitable impurities.
2. A copper-based alloy having excellent blanking die wear resistance, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, 0.001 to 0.02 weight % of C, and the balance of Cu and inevitable impurities.
3. A copper-based alloy as claimed in claim 1 or 2, having excellent blanking die wear resistance, wherein the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.
4. A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si in a total amount of 0.0007 to 0.5 weight %, and the balance being Cu and inevitable impurities.
5. A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 8 to 0.08 weight %, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and the balance being Cu and inevitable impurities.
6. A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Si, and the balance being Cu and inevitable impurities.
7. A copper-based alloy having excellent blanking die wear resistance and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.50 weight % of Zn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and 0.0007 to 0.5 weight % of Si, and the balance being Cu and inevitable impurities.
8. A copper-based alloy as claimed in any of claims 4, 5, 6, and 7, having excellent blanking die wear resistance and resin adhesion, wherein C is contained in an amount of 0.001 to 0.02 weight %.
9. A copper-based alloy as claimed in any of claims 4, 5, 6, 7 and 8, having excellent blanking die wear resistance and resin adhesion, wherein the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.
10. A copper-based alloy sheet formed of the copper-based alloy as claimed in any of claims 1, 2, 3, 4, 5, 6, 7, 8, and 9.
11. A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to

0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, 0.0005 to 0.02 weight % of C, and the balance of Cu and inevitable impurities.

12. A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, 0.001 to 0.02 weight % of C, and the balance of Cu and inevitable impurities.
13. A copper-based alloy as claimed in claim 11 or 12, having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, wherein the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V, and Mo is limited to less than 0.01 weight %.
14. A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing one or two or more elements selected from the group consisting of Al, Be, Ca, Cr, Mg and Si in a total amount of 0.0007 to 0.5 weight %, and the balance being Cu and inevitable impurities.
15. A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and the balance being Cu and inevitable impurities.
16. A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance and solderability, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Si and the balance being Cu and inevitable impurities.
17. A copper-based alloy having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, comprising 1.5 to 2.4 weight % of Fe, 0.008 to 0.08 weight % of P, 0.01 to 0.5 weight % of Zn, 0.003 to 0.5 weight % of Ni, 0.003 to 0.5 weight % of Sn, and 0.0005 to 0.02 weight % of C, and further containing 0.0007 to 0.5 weight % of Mg, and 0.0007 to 0.5 weight % of Si, and the balance being Cu and inevitable impurities.
18. A copper-based alloy as claimed in any of claims 14, 15, 16 and 17, having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, wherein C is contained in an amount of 0.001 to 0.02 weight %.
19. A copper-based alloy as claimed in any of claims 14, 15, 16, 17 and 18, having excellent blanking die wear resistance, repeated bending fatigue resistance, solderability, and resin adhesion, wherein the total content of one or two or more elements selected from the group consisting of Nb, Ti, Zr, Ta, Hf, W, V and Mo is limited to less than 0.01 weight %.
20. A copper-based alloy sheet formed of the copper-based alloy as claimed in any of claims 11, 12, 13, 14, 15, 16, 17, 18 and 19.

FIG.1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/01116

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ C22C9/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ C22C9/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 10-17956, A (Mitsubishi Materials Corp.), 20 January, 1998 (20. 01. 98), Column 3, line 30 to column 4, line 37 (Family: none)	1, 2, 10
A	JP, 7-242965, A (Mitsubishi Materials Corp.), 19 September, 1995 (19. 09. 95), Claims ; column 3, line 44 to column 4, line 7 (Family: none)	1-20
A	JP, 62-93325, A (Tamagawa Metal & Machinery Co., Ltd.), 28 April, 1987 (28. 04. 87), Claims ; page 3, upper right column, line 9 to lower left column, line 3 (Family: none)	4, 5, 8, 10
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 May, 1999 (13. 05. 99)		Date of mailing of the international search report 25 May, 1999 (25. 05. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/01116

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 62-70541, A (Mitsubishi Metal Corp.), 1 April, 1987 (01. 04. 87), Claims & US, 4749548, A & US, 4872048, A & GB, 8621958, A0 & GB, 8907058, A0 & GB, 2181742, A1 & GB, 2219473, A1 & GB, 2181742, B2 & GB, 2219473, B2 & DE, 3631119, A1	4-10, 14-20

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